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Study of Type II and Type III Anodized Al 5052-0 in Aqueous DS2 Solutions

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Study of Type II and Type III Anodized Al 5052-0 in Aqueous DS2 Solutions

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Corrosion behavior studies using short-time electrochemical techniques and long-term immersion tests of Types II and III anodized Al 5052-0 and uncoated Al 5052-0 were conducted in 30 vol% DS2 aqueous decontaminating solution. Test data indicated that Type III anodized Al 5052-0 provided significantly greater resistance to degradation than Type II anodized Al 5052-0 or uncoated Al 5052-0.

The System Engineering Division, U.S. Army Tank-Automotive Command (Warren, Michigan) requested the U.S. Army Materials Technology Laboratory's (MTL) assistance in assessing the corrosion resistance of two types of anodic coatings for the Al 5052-0 (UNS A95052) alloy housing cover of the Bradley turret drive system when exposed to the decontaminating agent DS2. The housing cover is currently being treated with the Type III hard anodic coating in accordance with MIL-A-8625E. The General Electric Company, responsible for the turret drive system, has proposed as a cost-savings measure, that the Type III hard anodic coating be replaced with the Type II conventional anodic coating produced from the sulfuric acid bath. The Corrosion Science Team at MTL has developed a technical data base for a variety of metals, alloys, and metal matrix composites listing their compatibility

with DS2 and other decontaminating agents using short-term electrochemical and long-term immersion tests. However, data for the Al 5052-0 alloy and this anodically coated alloy had not been obtained. Accordingly, the objective of this program was to assess and compare the performance of Al 5052-0 when protected by either of the MIL-A-8625E Types II and III anodic coatings after exposure to DS2 decontaminating agent.

Prior experimental work at MTL on the compatibility of aluminum alloys with DS2 showed that a marked increase in corrosion rate occurs when the DS2 agent is diluted with H₂O.¹ It is reasonable to expect that moisture or water will be introduced into the DS2 agent in field service, particularly under combat conditions. As a consequence, an aqueous solution of DS2 was used in this study to represent a worst-case scenario.

Aluminum is essentially non-reactive near pH 7, but its electrochemical activity in aqueous solutions increases rapidly on either side of this neutral point. The corrosion reaction on the acid side involves dissolution of aluminum with the evolution of hydrogen:



The reaction on the basic side forms aluminate anions and liberates hydrogen:



Factors that control metallic corrosion can be categorized as thermodynamic or kinetic. Thermodynamics determine tendency to corrosion; that is, whether or not a reaction is possible. The electrochemical principles of thermodynamics are those of reversible cells and standard potential. Application of these principles shows that most materials can react with their environments.

The important engineering question is how fast will they react, which is the basis for the study of kinetics of corrosion reactions. Polarization techniques are particularly well suited for the study of corrosion reaction kinetics. These tech-

niques are faster and more sensitive than conventional corrosion tests. They allow each of the partial processes in the corrosion reaction to be studied independently of the others. Polarization techniques have been used to study the effect of a variety of factors on the corrosion behavior of metals and alloys: the effects of composition, microstructure, heat treatment, and strength level. In potentiostatic polarization, by making the potential rather than the current the independent variable, it is possible to study the dissolution behavior of the alloy over its entire potential range.

In this study, rapid potentiodynamic scans were performed over a very limited potential range (generally -100 to 100 mV from the corrosion potential) to determine the corrosion rate of the underlying alloy due to the microporosity and permeability of the oxide film. The long-term immersion tests performed provide supporting corrosion rate and oxide film data based on weight loss measurements and metallographic analysis. Immersion tests, weight loss, and metallographic studies were performed to determine the rates of anodized layer (oxide) degradation and dissolution and the rate of metal alloy corrosion.

Materials and Procedures

Two housing covers were provided by the General Electric Company (Pittsfield, Massachusetts). These housing covers were fabricated of annealed Al 5052-0 (SPEC QQ-A-250/8) and had a thickness of 0.090 ± 0.004 in. (2.29 ± 0.10 mm). Table 1 contains the nominal chemical analysis of the alloy in weight percent.

The first housing cover received a hard anodic coating in accordance with MIL-A-8625 Type III, Class 2, black and hot water seal $0.0025 + 0.0010$ or -0.0000 in. ($0.0635 + 0.0254$ or -0.0000 mm) thick. The second housing cover was given an anodic coating in accordance with MIL-A-8625, Type II, Class 2, black, 0.0004 in. (0.010 mm) minimum thickness.

The corrosion behavior of uncoated Al 5052-0 and the alloy coated with Types II and III anodized films was studied by anodic and cathodic potentiostatic polarization tech-

Si	Fe	Cu	Mn	Mg	Cr	Zn	Others		Al
							Each	Total	
0.25	0.40	0.10	0.10	2.2-2.8	0.15-0.35	0.10	0.05	0.15	Rem

NOTE: Composition in percent maximum unless shown as a range or minimum

niques and by long-term immersion tests as a function of time at room temperature.

A Pyrex[®] cell with a volume of one liter containing 500 mL of DS2 agent with water added was utilized for potentiodynamic scans. The composition of the DS2 decontaminating solution was 70 wt% diethylenetriamine, 28 wt% methyl cellosolve (ethylene glycol monomethyl ether), and 2 wt% sodium hydroxide.

Previous work showed that the maximum corrosion rate for aluminum alloys occurred in about 30 vol% DS2. As a consequence, this highly corrosive solution (pH 12) was used in this investigation.

The important engineering question is how fast will they react, which is the basis for the study of kinetics of corrosion reactions.

The reference electrode was a saturated calomel electrode (SCE) separated by a glass bridge with a Vcor tip. The working electrode disk was contained in a polytetrafluoroethylene holder and had an exposed surface area of 1.0 cm^2 . The electrochemical cell has been described in detail elsewhere. In order to describe the anodic and cathodic processes, anodic and cathodic polarization measurements were made using the potential sweep method of potentiodynamic polarization. To minimize alteration of surface, the electrode potential was continuously changed at a rapid constant rate of $5,000 \text{ mV/h}$, and current was simultaneously recorded. For Al 5052-0, a density of 2.68 g/cm^3 was used.

[®]Trade name.

A 100 mL glass jar containing 80 mL of DS2 solution was utilized for immersion tests. The test specimen disk was contained in a polytetrafluoroethylene holder which exposed a surface area of 1.0 cm^2 . Measurements of total weight loss in mg/cm^2 were made vs immersion time in hours.

Results and Discussion

Potentiodynamic Polarization—Uncoated Al 5052-0

Figure 1 shows a potentiodynamic scan for the uncoated alloy after 10 minutes immersed in DS2 solution. Because the anodic and cathodic scans for the alloy after longer immersion times (not shown) were made within the same potential range, the curves were quite similar. The anodic curve shows active dissolution with no tendency to passivate and a maximum observed current density of $\sim 1,800 \mu\text{A/cm}^2$.

Table 2 lists the maximum observed current densities for the uncoated alloy as a function of immersion time in the DS2 solution. The maximum observed current densities were high and ranged approximately from $1,700$ to $1,800 \mu\text{A/cm}^2$.

Type II Anodized Al 5052

Figure 2 contains potentiodynamic scans for the Type II anodized alloy after different immersion times in DS2 decontaminating solution. Comparing these curves with those of the bare aluminum alloy in Figure 1, it is clear that the Type II anodic coating, after immersion times of 10 and 30 minutes, shifts the corrosion potential in the noble direction and significantly reduces the maximum observed current density from $\sim 1,800 \mu\text{A/cm}^2$ to less than $30 \mu\text{A/cm}^2$, which is typical of passivity. However, after immersion times of 60 to 240 minutes, there are marked

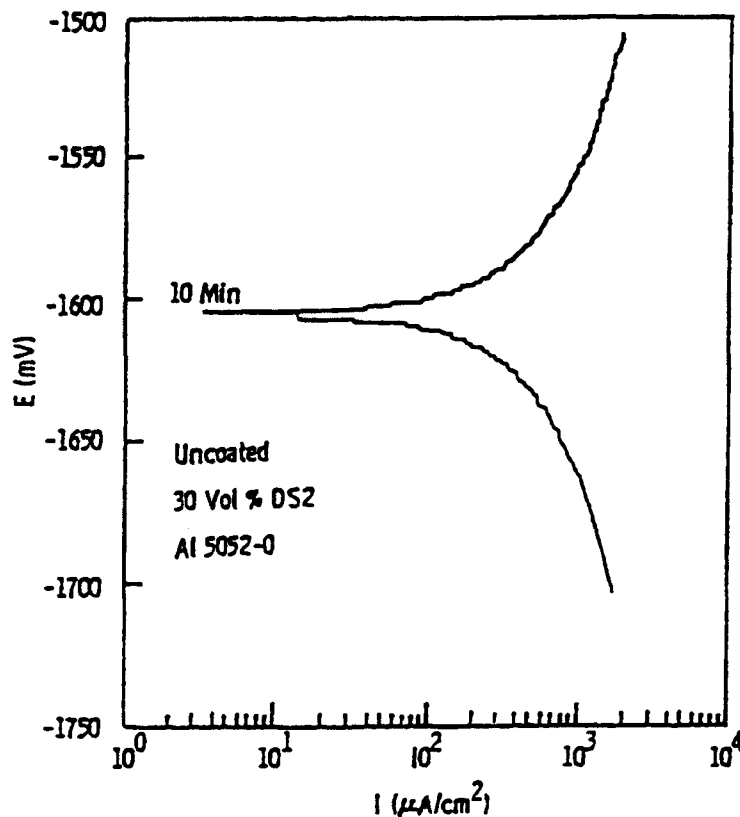


FIGURE 1

Potentiodynamic polarization curve of uncoated Al 5052-0 after 10 min immersion in 30 vol% DS2 at 25 °C. Scan rate: 1.388 mV/s.

TABLE 2

Potentiodynamic Potential Ranges, Corrosion Potentials, and Maximum Observed Current Densities for Uncoated Al 5052-0 in 30 vol% DS2

Immersion Time (min)	Initial E to Final E (mV)	E_{corr} (mV)	Maximum Observed Current Density ($\mu\text{A}/\text{cm}^2$)
10	-100 to 100	-1605	1800
30	-100 to 100	-1597	1800
60	-100 to 100	-1597	1800
80	-100 to 0	-1596	
100	-100 to 0	-1591	
120	-100 to 100	-1585	1800
240	-100 to 100	-1573	1700

changes: the corrosion potential and magnitude of the current density approach those of the uncoated alloy, indicative of dissolution of the protective anodic film. The maximum observed current densities determined from the polarization curves in Figure 2 are contained in Table 3. The anodic protective layer was still present and effective after 10 and 30 minutes immersion. How-

ever, after 60 minutes of immersion time, the maximum observed current density markedly increased to $\sim 1,800 \mu\text{A}/\text{cm}^2$, indicative of dissolution of the anodic layer.

Type III Anodized Al 5052-0

Figure 3 shows polarization curves for the alloy protected with the Type III hard anodic coating after immersion times of up to 120

minutes in DS2 solution. The anodic curves after 10, 30, and 60 minutes of immersion time are similar and are characterized by significantly more noble corrosion potentials and lower maximum observed current densities ($\sim 1 \mu\text{A}/\text{cm}^2$), indicative of the superior nature of the Type III hard anodic coating when compared to the Type II anodic coating. However, after 120 minutes of immersion time in DS2 solution, the corrosion potential became much more active and the maximum observed current density increased to $\sim 100 \mu\text{A}/\text{cm}^2$, which is lower than the maximum observed current density of $\sim 1,800 \mu\text{A}/\text{cm}^2$ developed for the Type II coating after the same immersion time. Extending the immersion time to 240 minutes served only to shift the corrosion potential in the more active direction to the same corrosion potential as the uncoated alloy. The maximum observed current density, however, remained at $\sim 100 \mu\text{A}/\text{cm}^2$, which is considered to be the limit for passivity. Further increases in immersion time up to 420 minutes produced no changes in corrosion potential, but the maximum observed current density decreased to $65 \mu\text{A}/\text{cm}^2$. A photomicrograph of the coated alloy surface taken after nine hours of immersion time shows that a significant amount of the Type III hard anodic coating is still present. The maximum observed current densities for the Type III anodized Al 5052-0 determined from the polarization curves of Figures 3 through 5 are contained in Table 4. These maximum observed current densities were markedly lower than those for the uncoated alloy and the Type II anodized alloy at comparable immersion times.

Long-Term Immersion Tests for Uncoated Al 5052-0

Figure 4 is a plot of total weight loss in mg/cm^2 vs hours of immersion for uncoated Al 5052-0 disk specimen exposing one cm^2 of surface area to the 30 vol% DS2 solution. A linear relationship is observed and the rate of weight loss is approximately constant at about $2.5 \text{ mg}/\text{cm}^2/\text{h}$.

At 5X magnification, machining marks were evident on the surface of an uncoated Al 5052-0 specimen prior to immersion. For the same

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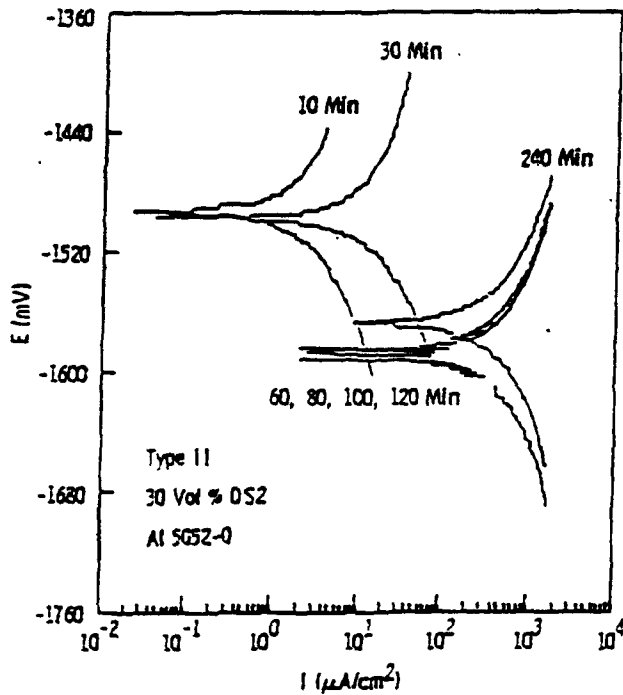


FIGURE 2

Effect of time of immersion on the potentiodynamic polarization behavior of Type II anodized Al 5052-0 in 30 vol% DS2 at 25°C. Scan rate: 1.388 mV/s.

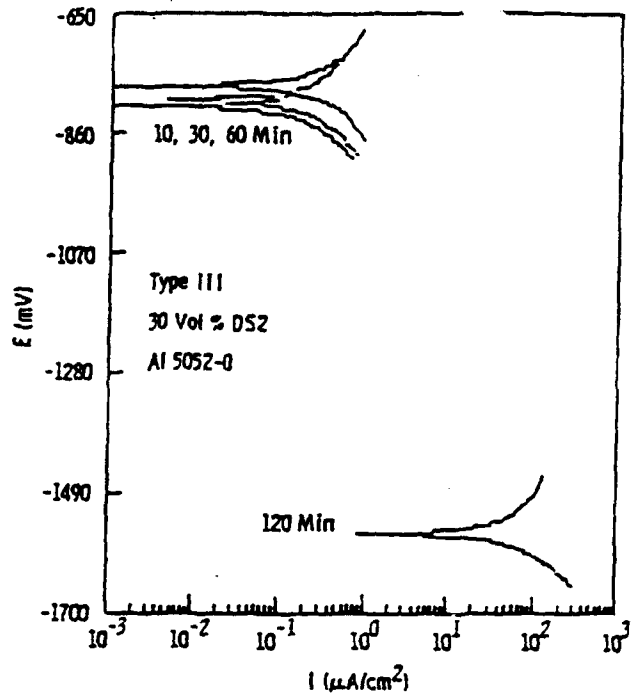


FIGURE 3

Effect of time of immersion up to 120 min on the potentiodynamic polarization behavior of Type III anodized Al 5052-0 in 30 vol% DS2 at 25°C. Scan rate: 1.388 mV/s.

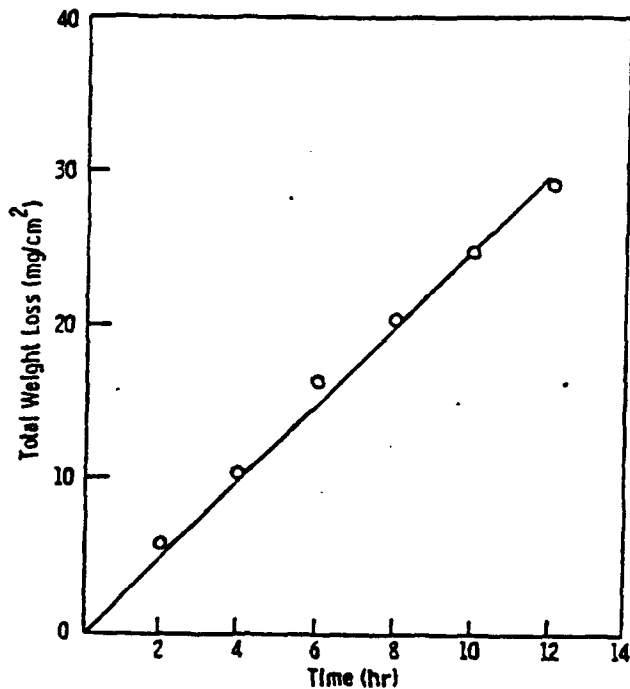


FIGURE 4

Effect of time of exposure on total weight loss for uncoated Al 5052-0 in 30 vol% DS2.

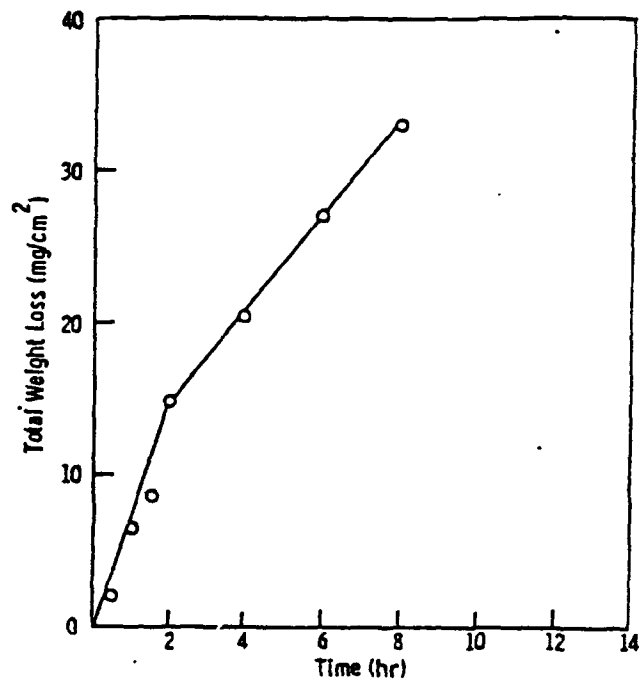


FIGURE 5

Effect of time exposure on total weight loss for Type II anodized Al 5052-0 in 30 vol% DS2.

TABLE 3

Potentiodynamic Potential Ranges, Corrosion Potentials, and Maximum Observed Current Densities for Type II Anodized Al 5052-0 in 30 vol% DS2

Immersion Time (min)	Initial E to Final E (mV)	E _{corr} (mV)	Maximum Observed Current Density ($\mu\text{A}/\text{cm}^2$)
10	-100 to 100	-1523	8.0
30	-100 to 100	-1501	30.0
60	-100 to 100	-1588	1800
80	-100 to 100	-1590	1800
100	-100 to 100	-1592	1800
120	-100 to 100	-1589	1800
240	-100 to 100	-1568	1800

TABLE 4

Potentiodynamic Potential Ranges, Corrosion Potentials, and Maximum Observed Current Densities for Type III Anodized Al 5052-0 in 30 vol% DS2

Immersion Time (min)	Initial E to Final E (mV)	E _{corr} (mV)	Maximum Observed Current Density ($\mu\text{A}/\text{cm}^2$)
10	-100 to 100	-778	1.0
30	-100 to 100	-800	0.8
60	-100 to 100	-807	0.8
120	-100 to 100	-1555	120
180	-100 to 100	-1588	100
240	-100 to 100	-1599	150
300	-100 to 100	-1605	65
360	-100 to 100	-1608	65
420	-100 to 100	-1610	65
540	-100 to 100	-1615	55

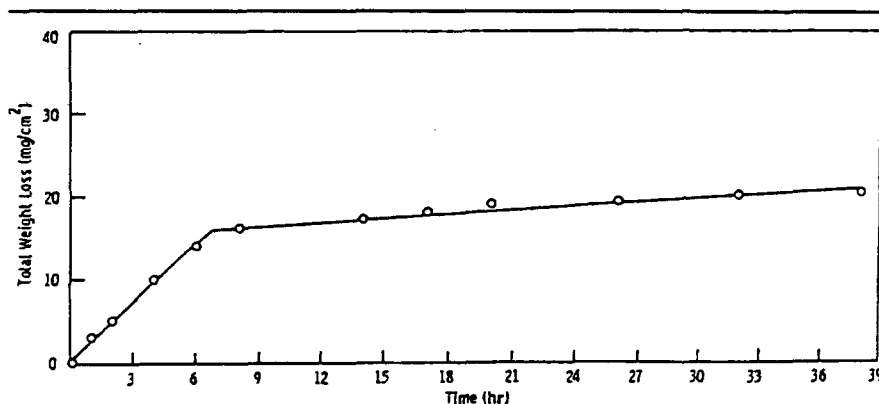


FIGURE 6

Effect of time of exposure on total weight loss Type III anodized Al 5052-0 in 30 vol% DS2.

specimen surface after 12 hours immersion time, the machining marks disappeared, reflecting the relatively large weight loss of the alloy due to corrosion.

Type II Anodized Al 5052-0

Figure 5 plots total weight loss as a function of immersion time. The initial linear rate of increase of weight loss up to two hours of immersion time is high and corresponds to a rate of weight loss of 7.5 mg/cm²/h due to the rapid dissolution of the Type II anodized coating. After two hours immersion time, the rate of weight loss decreases to 0.05, that which is roughly equivalent to the rate of the uncoated alloy. Metallographic examination was consistent with the weight loss data. The surface of the as-received Type II black anodized Al 5052-0 disk at 5X magnification prior to immersion became a mottled gray after one and

one-half hours of immersion time, respectively. After two hours of immersion time, the gray coating was no longer present.

Type III Anodized Al 5052-0

Weight loss data for the Type III anodized alloy is shown in Figure 6. The initial relatively high dissolution rate of the Type III hard anodic coating diminishes significantly after eight hours immersion time. The rate of total weight loss and the corrosion rates are markedly below those for the Type II anodized Al 5052-0 and the uncoated alloy.

Conclusions

The potentiodynamic polarization tests, the long-term immersion tests, and metallographic examination show:

- The uncoated alloy has a very high maximum observed current density of $\sim 1,800 \mu\text{A}/\text{cm}^2$ when ex-

posed to the DS2 decontaminating solution and will require a protective coating.

- The Type II anodic coating dissolves after about one hour of exposure to DS2 solution, after which a maximum observed current density equivalent to that of the uncoated alloy is observed.
- The Type III hard anodic coating was protective after two hours of exposure. Although some dissolution occurred thereafter, the coating was still present on the alloy surface after eight hours of exposure to DS2 solution. Weight loss and electrochemically determined maximum observed current densities were markedly lower than those of both the Type II coated alloy and the uncoated alloy.
- The performance of the Type III hard anodic coating was markedly superior to that of the Type II anodic coating in an aqueous DS2 solution representing the worst case scenario, and it is, therefore, recommended for the application.

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1. C. Zabielski, M. Levy, and J. Scanlon, Corrosion and Corrosion Inhibition of Metals: Alloys in Methylphosphonic Difluoride and Decontaminating Solutions, U.S. Army Materials Technology Laboratory, MTL TR 89-61, July 1989.
2. M. Levy, Corrosion, 23, 8 (1967): p. 237.

More information may be available from CORROSION/92 paper no. 467, presented in Nashville, Tennessee.

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